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Characterization and Degradation Studies on Synthetic
Polymers for Aerospace Application

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NASA

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Polymers for Aerospace Application

Final Report (Oct. 1, 1981 - Dec. 10, 1982)

by

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Moffett Field, California 94035

SUMMARY

The research carried out during the past fourteen months has been concerned
with the characterization and degradation of polymers for aircraft applications.
Two phases of research are presented in the final report on NASA-Ames Cooperative
Agreement No. NCC 2-28. Phase one of the research is the characterization and
degradation of candidates for antimisting fuel additives. Phase two of the
research is the characterization and thermal degradation of composite resins.

INTRODUCTION

As part of the overall pr :ram of fire control in aircraft, recent studies have included attempts to control fire caused by fuel-tank and fuel-line rupture following collision - part of the so-called post crash fire containment program. These attempts have concentrated on making the fuel "safe" when released inadvertently from the tanks. Currently, this has involved adding to the fuel a compound that essentially minimizes fuel volatility or resists the formation of small droplets, and is often known as a so-called "anti-misting" additive. Characterization of a good anti-misting compound is difficult since presently it is not known which properties directly control or even contribute to such volatility control in jet fuels. Moreover, in the absence of criteria to describe such phenomena, it is difficult to optimize the properties of such a species. This further complicates our ability to refine presently available materials, or to design and synthesize new materials, such that when they are added to jet fuel, they will provide an essentially non-flammable fuel when released accidentally from a ruptured tank, and yet which will burn efficiently when required to provide good engine performance under normal circumstances.

Characterization of the fuels modified by anti-misting additives (AMA) is a function of both chemical and physical parameters, and the usual chemical structure determinations via conventional methods such as NMR, IR, GC/MS, elemental analysis, and other techniques, have been employed. The data for AMA chemical structure determinations are not required to report at this time. In addition, both static and dynamic characterization of the AMA modified fuel via surface tension, viscosity, specific gravity, and other physical parameters have been carried out. In particular, changes in such parameters after sub-jection of the AMA modified fuel to a severe sequence of mechanical stresses have been attempted. The droplets formation upon impact for fuels modified by AMA have also been studied, and thus provide confirmation that the AMA really does modify the behavioral patterns of the fuel in scenarios involving impact and sudden accelerations (simulation modelling of crash events).

The final report includes the characterization of FM9, polyisobutylene and their modified fuels. Synthesis alternative AMA candidates have been attempted. Some data for alternative AMA is shown in the Appendix.

EXPERIMENTAL RESULTS - A.CHARACTERIZATION OF FM9

ISOLATION/QUANTITATION OF ANTI-MISTING ADDITIVES FROM KEROSENE TYPE FUELS

This procedure was taken from notes supplied by Dr. J. Knight
of the Royal Aircraft Establishment at Farnborough, England.

40-50 g of FM9 fuel in kerosene are accurately weighed into a 1-litre conical flask. Absolute ethanol (ca. 200 ml) is added to the fuel in portions, swirling the solution between each addition to achieve good homogeneity. Methanol is then added to the flask in portions and the contents are kept agitated between each addition. Methanol addition is continued until about 1 litre of turbid colloidal solution is present in the flask. This should be completely homogeneous and should not contain any macroscopic particles of precipitate. A 0.1% solution of calcium chloride in methanol is then added until coagulation of the FM9 particles begins. The mixture is shaken vigorously for 5-10 mins then allowed to settle for a least 12 hours. The majority of FM9 should have precipitated as a fibrous, very slightly swollen solid, and the mother-liquor should be clear. The contents of the flask are then filtered carefully onto a preweighed Millipore PTFE filter of 10 micron pore size (recommended 47 mm diameter), using slight suction. Stirring of the mixture should be avoided so that the bulk of the liquid can be quickly filtered, transferring any methanol washings to the filter until all solid has been collected. The precipitate is then allowed to dry in the air to constant weight and its weight recorded.

EXAMPLE: 4.0 g of FM9 solution weighed into flask; weight of filter was 138 mg initially and 250 mg after precipitation, giving 112 mg of FM9 solid. Hence concentration of FM9 in kerosene fuel was 0.28%.

NOTES: When the base kerosene is very low in aromatics or has a particularly high boiling range, it may be necessary to increase the proportion of ethanol used so as to prevent immiscibility of the fuel with the alcohol mixture. Separation of kerosene after addition of alcohols should be avoided because the FM9 precipitates in a gelatinous form and is swollen by the kerosene, making it much more difficult to dry out.

Elemental Analyses:

The solid anti-misting additive (FM9) was isolated from the Jet A kerosene fuel by conventional methods involving solvent precipitation and filtration. A detailed procedure for this process has already been given.

The solid FM9 was submitted to conventional elemental analysis (Huffman Laboratories, Inc., Colorado, 80033):

Carbon:	82.38%	82.12%
Hydrogen:	9.63%	9.53%
Oxygen:	6.16%	5.86%

Nitrogen:	less than 0.2%
Sulphur:	less than 0.2%
Phosphorus:	not assayed

Ash-residue:	approximately 2% (by difference)

Since the solid is precipitated in the presence of calcium chloride, the calcium metal content was determined by us via atomic absorption methods.

Found: Calcium 0.38% by weight

Standardization of the atomic absorption calibration curve for this spectrometer was done by reference to known % w/v solutions of calcium ion in water. The actual sample analysed was FM9 in a p-dioxane solution. Because of potential precipitation and evaporation effects prevalent in the aspiration and atomization process needed to feed the analyte to the flame, it is probable that this number of 0.38% calcium represents a minimum possible value for the calcium content.

Solubility of the FM 9 Solid (preliminary study):

The solubility of solid FM9, as isolated from Jet A kerosene, was determined for various organic solvents. Bearing in mind the possible conformational and structural changes that can occur on isolation as a polymeric solid from a kerosene based fuel, the solubilities found do not necessarily reflect the properties of the parent compound. No quantitative data for solubilities are available concerning particle size distributions in apparently homogeneous systems.

Observations:

A. The isolated FM9 solid derived from original Jet A kerosene fuels was insoluble in ethyl alcohol, n-hexane, and JP-5 kerosene fuel.

B. The isolated FM-9 solid "swelled" in chloroform, benzene, toluene and carbon tetrachloride solvents.

C. The isolated FM9 solid was slightly soluble in pyridine and benzaldehyde.

D. The isolated FM9 solid was partially soluble, more so than group C above, in p-dioxane, iso-butylamine and other primary amines.

E. When JP-5 fuel was added to iso-butylamine solutions of the solid FM9, the solid re-precipitated. It is suspected that the apparent low solubility of the originally fuel derived Jet A fuel solid FM9 in JP-5 fuel is partially attributable to the presence of calcium in the solid.

F. The solid FM9 derivative is much more soluble in commercially supplied p-dioxane, presumably containing significant quantities of peroxide, than it is in freshly distilled p-dioxane free of such impurities.

G. When freshly distilled p-dioxane was used as a solvent, the solid FM9 needed to be soaked for 7 days at 70°C in this solvent to effect solubilization to the extent of only 1 - 3% by weight. The resultant solution was opalescent and only marginally homogeneous; it would not pass through either a 0.5 or a 1.0 micron filter, but would pass a 10 micron filter.

H. The isolated solid FM9 did contain a small fraction of material soluble in toluene, presumably small molecular weight components, since the molecular weight distribution of toluene-extracted FM9 solid was different to that measured for the solid directly (see notes below on GPC measurements).

Molecular weight(MW)determination by gel permeation chromatography(GPC):

Conventional GPC analyses of apparent molecular weight distributions were conducted using Micro-Styragel® columns with 10,000 AU, 100,000 AU, and 1 million AU pore sizes, each connected together in sequence and eluted with p-dioxane. Various preparation methods were used to solubilize the FM9 additive prior to GPC analysis.

1. A parent curve and basic molecular weight (MW) distribution was determined for the FM9 dispersed as a 1.5% w/v solution in Jet A kerosene fuel (i.e. for material as received) using p-dioxane as an eluant A reasonably narrow MW distribution was found with a weight average value of 1,709,000 and a number average of 885,000. The ratio of weight average to number average molecular weights was 1.93 for this material; see Curve D in Figure 1 overleaf.

2. To determine whether shear stresses induced via a high speed paddle wheel ("blender" knives from a domestic blending machine) led to chain scission and thus molecular weight changes, this FM9 modified Jet A fuel (as re-

ceived directly) was subjected to 15 minutes agitation in a blender and then tested by GPC. Data are shown in Figure 1, Curve E, and indicate that the weight average molecular weight falls from 1.7 million to 813,000 and the number average MW decreased from 885,000 to 493,000 (ratio of 1.65).

3. It was also obvious that isolation procedures to obtain the FM9 derivative from Jet A solutions via solvent precipitation (vigorous shaking is also necessary) led to more than mere conformational changes, since GPC measurements on the isolated solid dissolved in p-dioxane (Curve B in Figure 1) show a weight average MW of 280,000 and a number average of 81,000 (ratio 3.45).

4. More interestingly, when the solid FM9 derived from Jet A fuel was subjected to toluene extraction procedures, GPC measurements of this extracted solid exhibited an apparent increase in molecular weight. This can only be attributed to extraction of lower molecular weight toluene-soluble components in the solid FM9 originally isolated from Jet A. The data are shown in Curve A, weight average MW of 486,000 and number average of 132,000 (ratio 3.69).

5. To check for chain scission in the solid material as a function of mechanical stress, a sample of the solid FM9 isolated from Jet A fuel was ground in a mortar and pestle and subjected to GPC analysis. Data are shown in Curve C of Figure 1, with a weight average MW of 144,000 and a number average MW of 50,000 (ratio 2.88).

These data are summarized in Table 1 and Figure 1.

Table 1. Molecular weight distributions* for FM9 as a function
of sample preparation technique.

FM9 Modified Jet Fuel Sample description**	Weight Average Mol wt	Number Average Mol wt	Mol wt ratio
Jet A fuel solution of FM9 as received	1,709,000	885,000	1.93
Jet A fuel solution after 15 minutes in blender	813,000	449,000	1.65
Solid FM9 (isolated from Jet A solutions) dissolved in p-dioxane	280,000	81,000	3.45
Toluene solvent-extracted solid FM9	486,000	132,000	3.69
FM9 solid after grinding in mortar and pestle	144,000	50,000	2.88

* Polystyrene samples were used to standardize the GPC measurements.

** Supplied as a 1.5% w/v solution of FM9 in Jet A kerosene fuel.

GEL PERMEATION CHROMATOGRAPHY MEASUREMENTS OF
MOLECULAR WEIGHT DISTRIBUTIONS FOR FM9

GPC COLUMN: STYRAGEL $(10^4/10^5/10^6$ AU in series)
PLOTTING SOLVENT: p-Dioxane
ELUTION RATE: 1 mL/minute
DETECTOR: UV Absorbance measurement
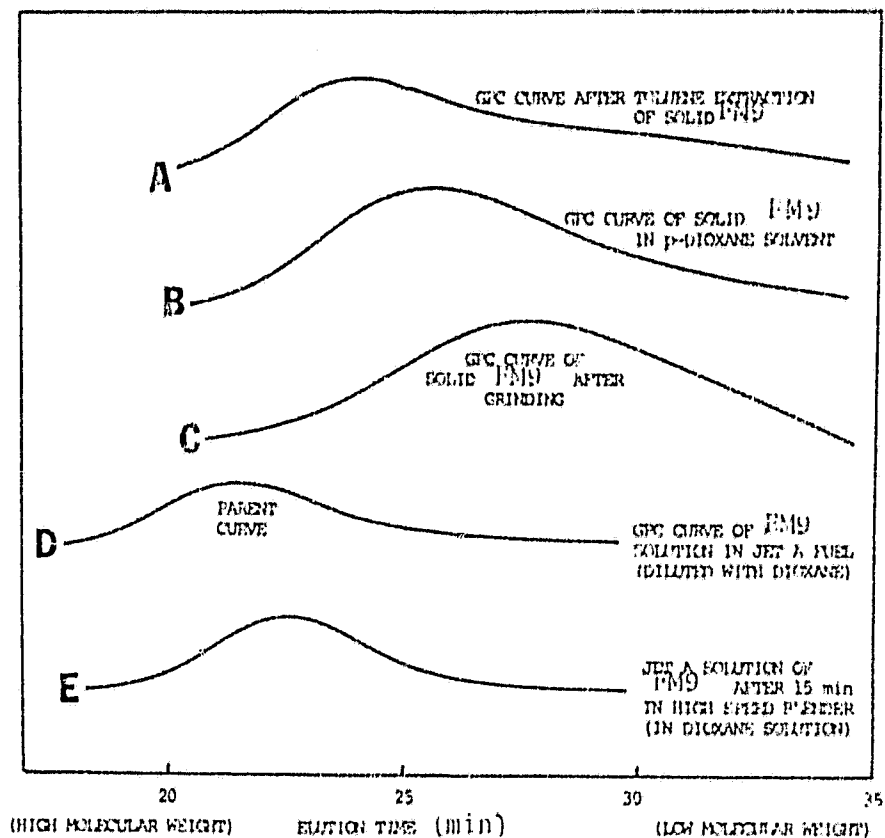TEMPERATURE: Room temperature

FIGURE 1

GEL PERMEATION CHROMATOGRAPHY MEASUREMENTS
FOR VARIOUS SAMPLES OF AN ANTI-MISTING ADDITIVE (FM9)
AS A FUNCTION OF THE PREPARATION PROCEDURE

Intrinsic viscosity measurements:

As a further test of the effects of mechanical stresses on the molecular weight distribution for the anti-misting additive FM9 the intrinsic viscosity of various solutions as a function of concentration (varied by diluting an initial 1.5% w/v solution provided) was measured. Measurements were made in a Model 100-D740 Viscometer at 25°C. Data are shown in Figure 2. In general, and as expected the larger the mechanical stress the smaller the overall measured molecular weight.

Specific gravity measurements:

Three samples of Jet A Kerosene based fuel containing FM9 were available:

A: A 0.3% w/v solution in Jet A received more than 12 months ago from the date of this measurement and stored in a loosely sealed container in the laboratory. Prior history was unknown.

B: A 0.3% w/v solution was received 4 months prior to the date of this measurement stored in laboratory in a loosely sealed container. Prior history was unknown.

C: A 1.5% w/v solution received approximately 12 months prior to the date of this measurement. Stored in a loosely sealed container under laboratory conditions. Prior history was unknown.
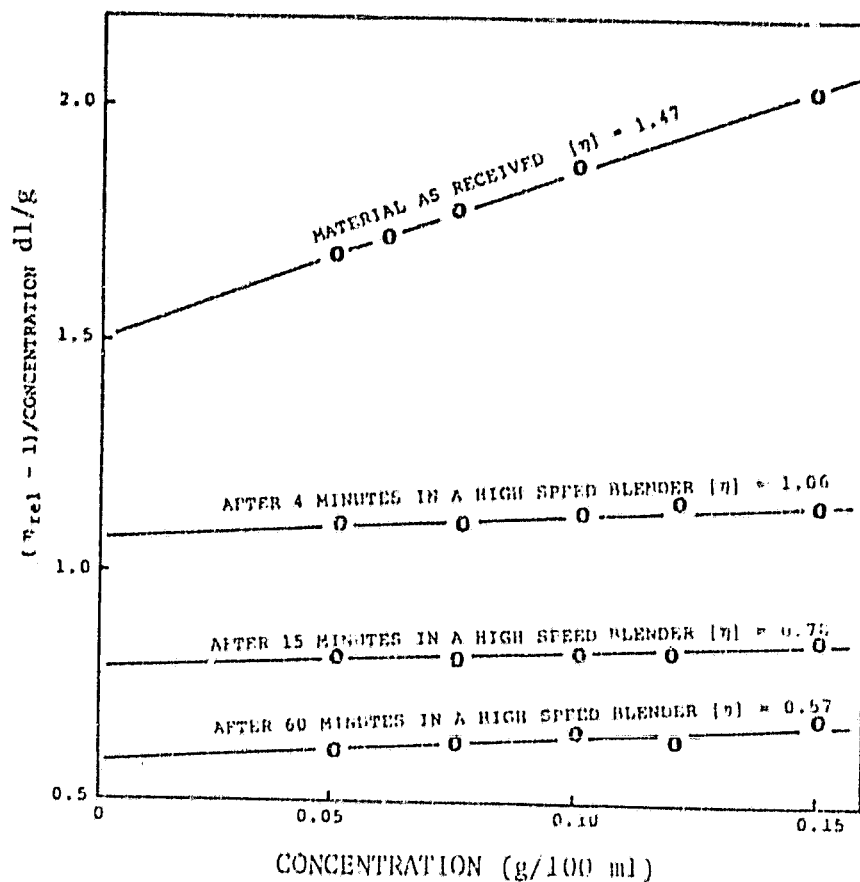
INTRINSIC VISCOSITY MEASUREMENTS FOR 1.5% BY
WEIGHT FM9 IN JET A FUEL DILUTED TO INDICATED
CONCENTRATIONS WITH JP-5 FUEL AT 25°C

FIGURE 2

THE EFFECT OF MECHANICAL STRESS ON THE
APPARENT MOLECULAR WEIGHT AS MEASURED BY THE
INTRINSIC VISCOSITY OF VARIOUS SOLUTIONS

Specific gravity measurements yielded the following data:

Sample A	As received	0.795
Sample B	As received	0.808
Sample C	Diluted to 0.3% w/v with Jet A kerosene	0.808
Jet A alone		0.810

Thus, 0.3% by weight for the FM9 is insufficient to change either the free volume or molecular packing ratios in the kerosene bulk fluid.

Surface tension measurements:

Since the purpose of the FM9 is to modify physical behavioral patterns following inadvertent release of fuel from its container (fuel tank rupture followed by high shear stress effects and probable dispersion as a mist or cloud of small droplets) then several physical parameters may be involved. It is already known that severe changes in fluid viscosity occur on shaking the FM9 modified fuel, and measurements by several groups have quantified this effect. A second possible parameter controlling anti-misting is surface tension. This parameter was measured by a standard du Nouy "ring" tensiometer, and the effects of shaking the FM9 modified fuel was assessed from surface tension coefficients. The following surface tension data were obtained at room temperature (24°C):

Jet A alone	25.9 dynes/cm.
0.3% w/v FM9 in Jet A	25.4 dynes/cm.
1.5% w/v FM9 in Jet A	25.7 dynes/cm.

A 1.5% w/v solution of FM9 in Jet A fuel was stirred with the aid of a magnetic stirrer.

After 5 minutes stirring	25.5 dynes/cm.
After 60 minutes stirring	23.0 dynes/cm.
After 120 minutes stirring	25.2 dynes/cm.

A 1.5 % w/v solution was stirred for 120 minutes and then allowed to relax, surface tension measurements were made as a function of time after cessation of the mechanical stress.

After 10 minutes	25.2 dynes/cm.
After 20 minutes	25.0 dynes/cm.
After 30 minutes	25.6 dynes/cm.
After 40 minutes	25.7 dynes/cm.

Admittedly, the relaxation time may be short, and significant changes may occur within seconds, rather than minutes. Thus, measurements made at times longer than the relaxation time after stressing will show no significant difference to values found for static systems. However, no significant changes could be discerned for static systems containing different quantities of FM9 Thus, this FMS species is not surface active at the concentrations indicated.
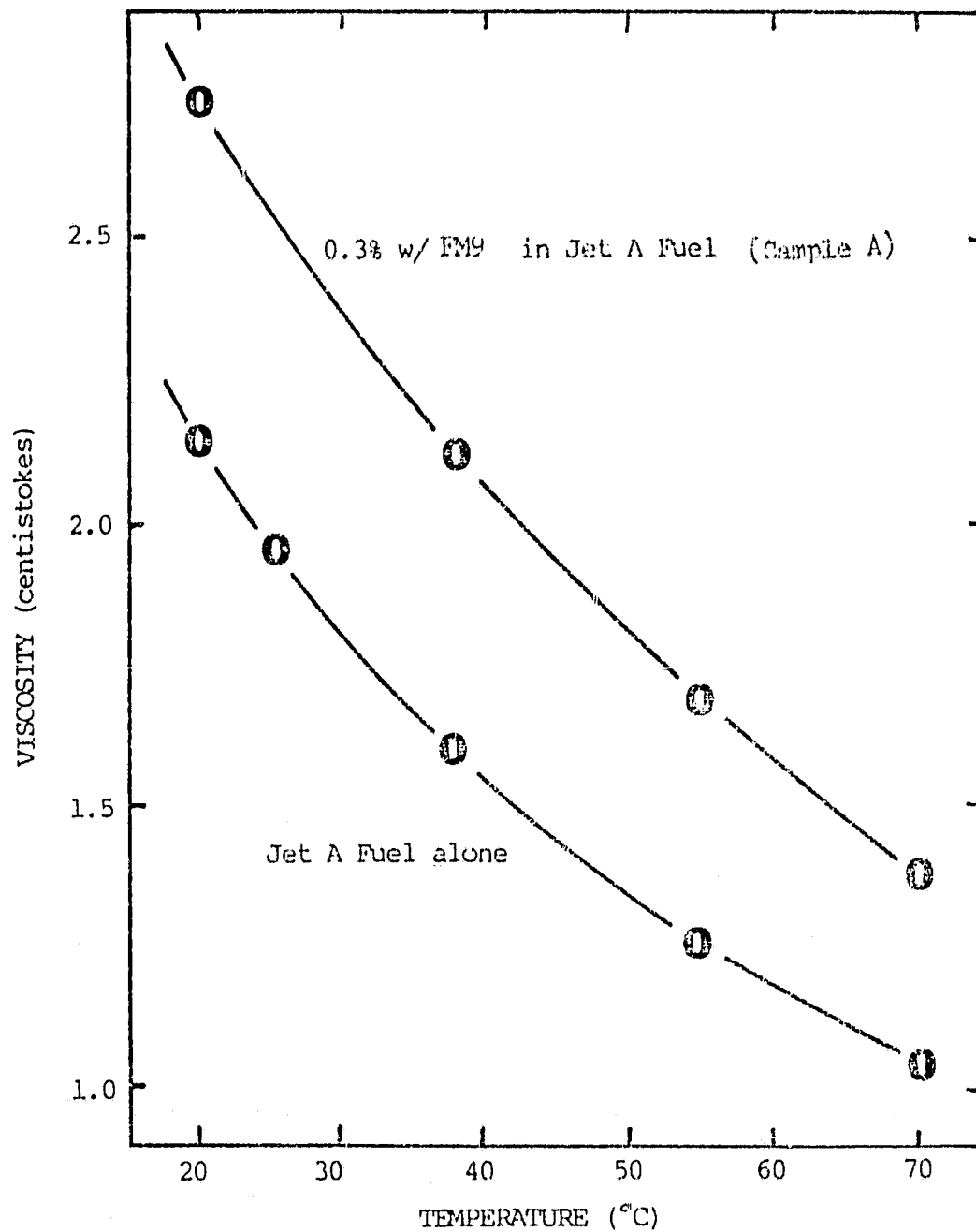
Viscosity measurements:

It is known that the viscosity coefficients for non-Newtonian liquids are a function of the shear stress used to induce viscous flow. Routine kinematic measurements of viscosity using a capillary flow technique will exhibit changes in this coefficient as the pressure "head" used to cause flow is altered. However, a limiting value for an infinitely small pressure will be a determinable parameter. Other groups are presently measuring viscosity coefficients as a function of shear stress, and we simply report conventional viscosity coefficients measured by standard techniques. These data are shown in Table 2 and Figure 3.

Table 2. Viscosity Coefficients for FM9 - Modified Kerosene Based Jet Fuel

| Sample | Temperature | | Viscosity Coefficient |
	°C	°F	(centi-stokes)
Jet A Fuel	20.0	68	2.12
	25.0	77	1.94
	37.8	100	1.57
	54.4	130	1.24
	71.1	160	1.02
0.3% w/w FM9	20.0	68	2.78
in Jet A fuel	37.8	100	2.11
(Sample A)	54.4	130	1.68
	71.1	160	1.36
0.3% w/w FM9	20.0	68	3.00
in Jet A fuel	25°C	77	2.70
(Sample B)	37.8	100	2.22
	54.4	130	1.78
	71.1	160	1.45
0.3% w/w FM9	25.0	77	3.10
in Jet A fuel by			
dilution from			
1.5% w/w (Sample C)			

Note: The intrinsic viscosity of Sample A at 25°C is 0.62 decilitres/gram,
for Sample B is 0.87 dl/g, and that for Sample C is 1.65 dl/g (Jet A solutions).

FIGURE 3

VISCOSITY MEASUREMENTS OF FM9 MODIFIED
KEROSENE BASED JET FUEL

Thermal Stability of FM9:

The thermogravimetric analysis trace for the solid FM9 isolated from the kerosene based Jet A fuel system is shown in Figure 4.

The differential scanning calorimetric trace for the kerosene fuel containing the FM9 is shown in Figure 5. The melting range is -47° to -42°C for the 1.5% w/v concentration solution.

UV/Visible absorption spectrum:

The solid FM9 isolated from the kerosene based Jet A fuel was dissolved in p-dioxane and the UV/visible absorption spectrum determined by double beam methods over the range 200 - 500 nm. The major feature is a well defined absorption maximum at 260 nm with an absorption coefficient of 181.4 optical density units at 1% concentration and for a 1 cm path length. Data are shown in Figure 6 (top figure).

Also shown in Figure 6 (bottom figure) is the absorption spectrum for FM9 modified fuel (Jet A), the only significant difference between this scan and that for the isolated solid re-dissolved in p-dioxane is the appearance of a small shoulder at approximately 285 nm that can be attributed to naphthalene contamination in the fuel itself.
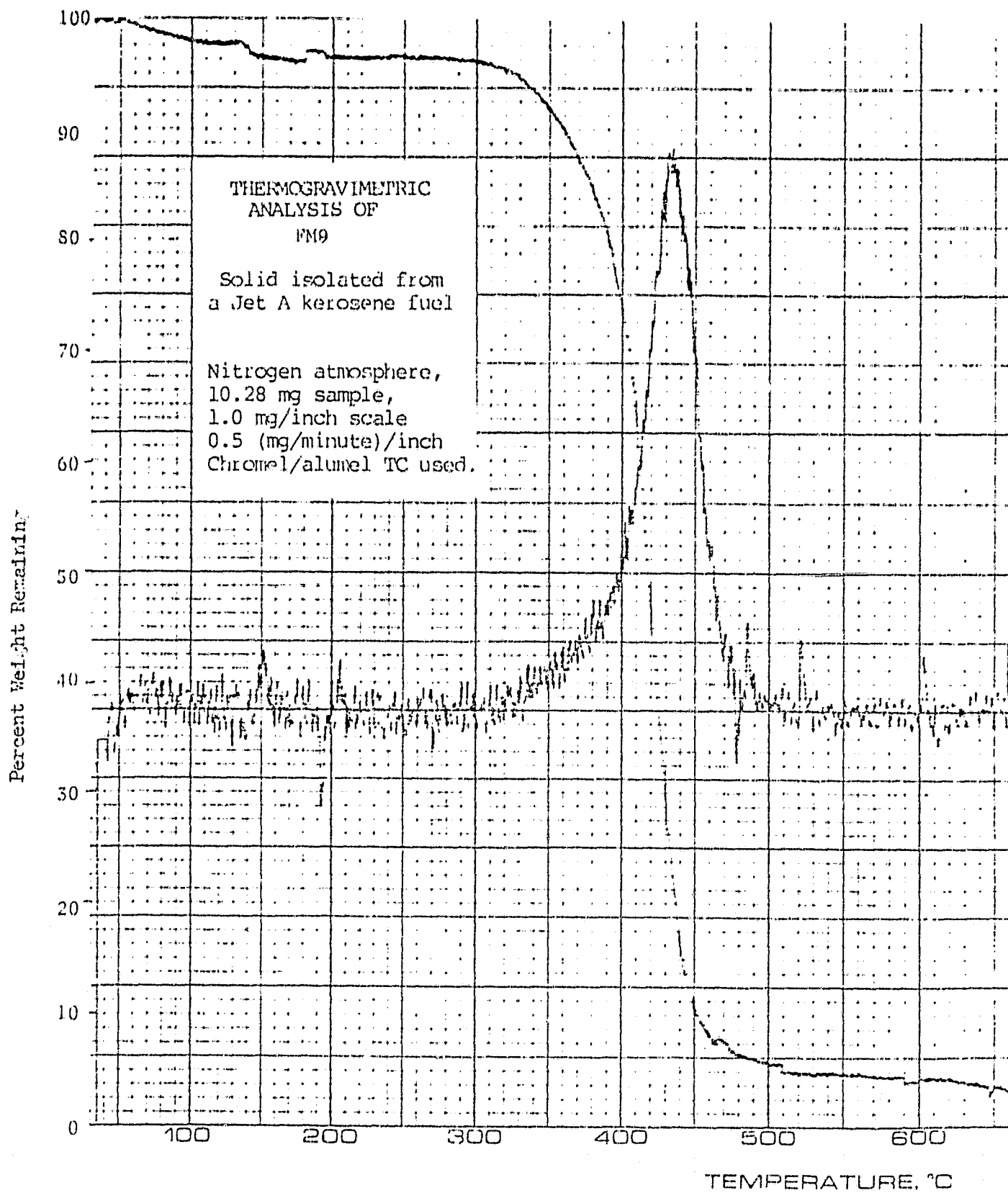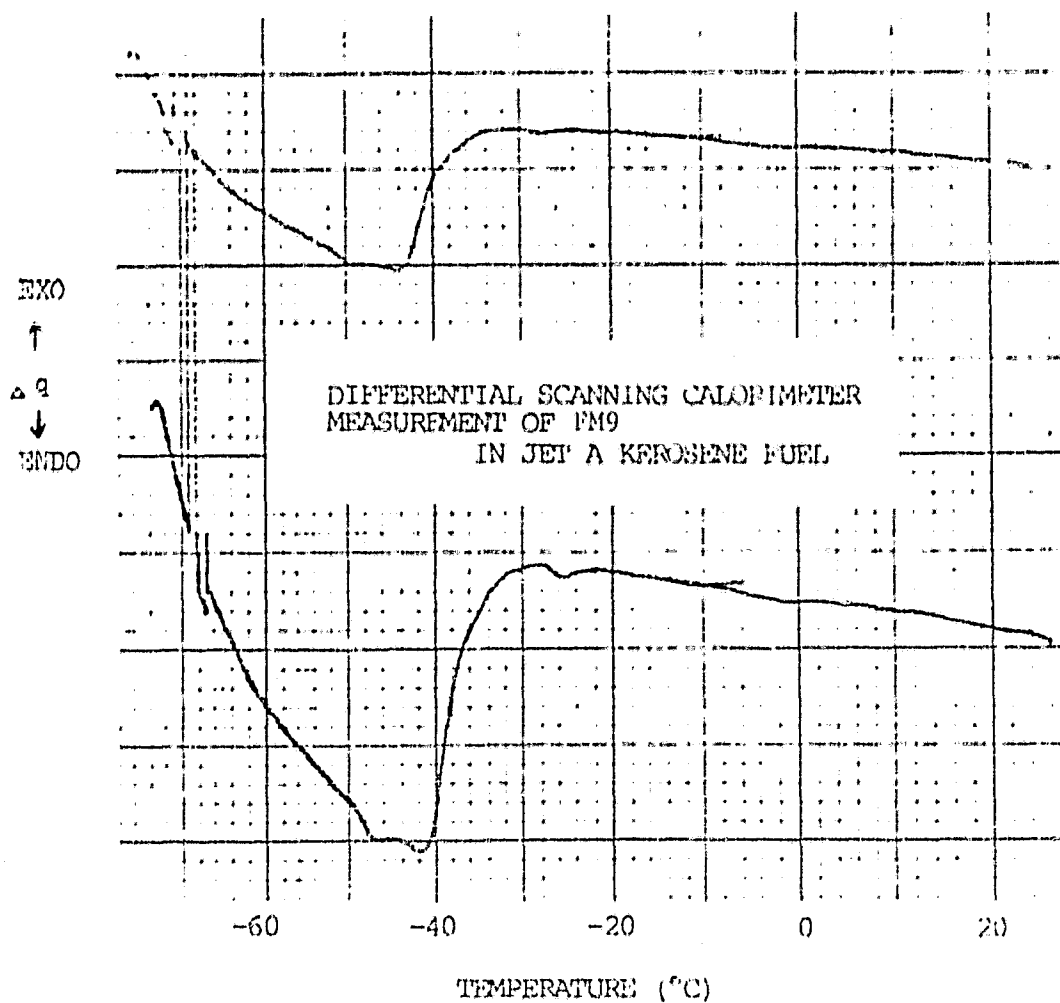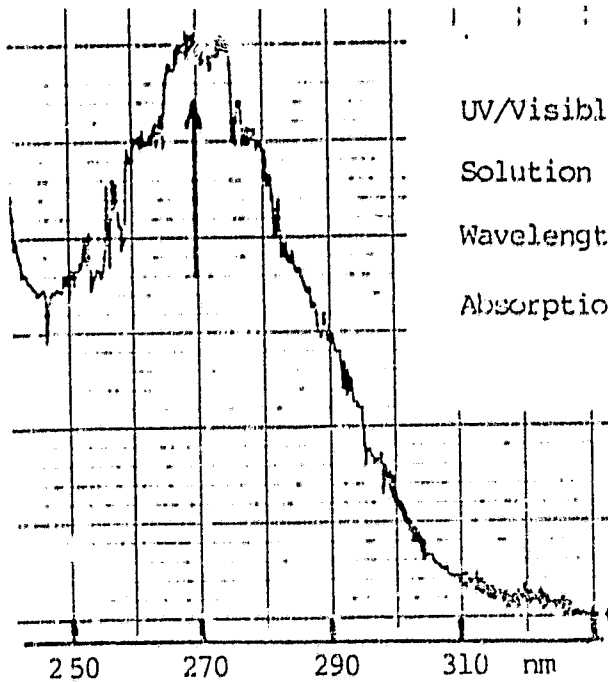
FIGURE 4

FIGURE 5

A DIFFERENTIAL SCANNING CALORIMETER
MEASUREMENT OF FM9
IN JET A KEROSENE FUEL

Additive concentration was 1.5% w/v in kerosene, the DSC run was
completed in a nitrogen atmosphere, and indicates a melting range
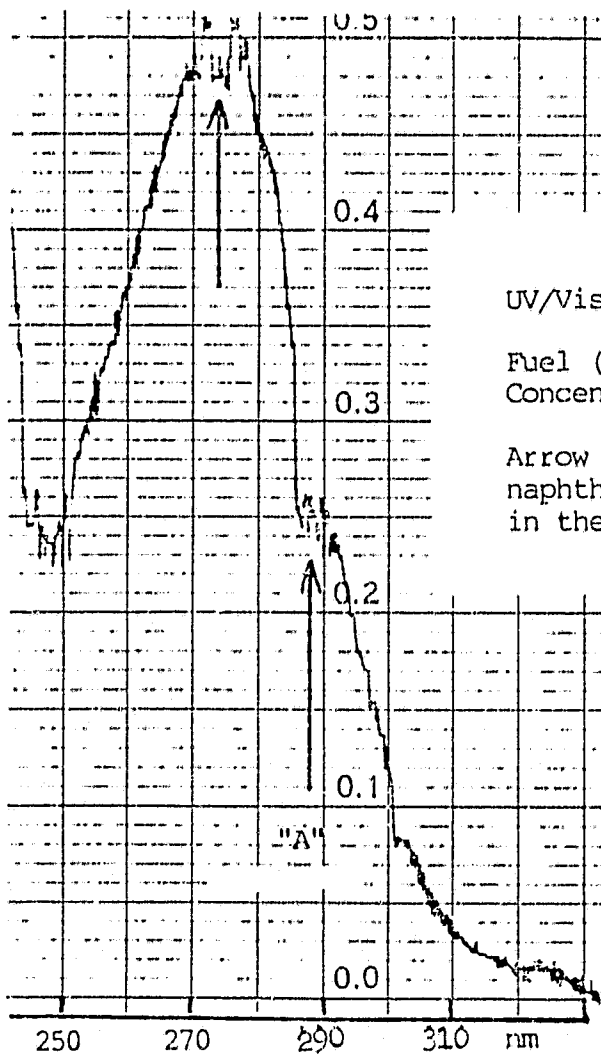for the fuel of between -47 and -42°C.

FIGURE 6

UV/Visible Absorption Spectrum of
FM9 in p-Dioxane
Solution at 0.25% w/v Concentration

Wavelength axis in units of nanometres

Absorption maximum at approximately 270 nm.

250   270   290   310   nm

UV/Visible Absorption Spectrum of
FM9 Modified Kerosene
Fuel (Jet A). Additive is at 0.3% w/v
Concentration.

Arrow at "A" indicates probable
naphthalene contamination at 285 nm
in the Jet A kerosene fuel itself.

0.5

0.4

0.3

0.2

0.1

"A"

0.0

250   270   290   310   nm

SUMMARY OF FM9 :

Initial and preliminary examination of this anti-misting additive FM9 with respect to its physical parameters discloses the following data:

Approximate weight average molecular weight in excess of 1.7 million, with a number average of 885,000.

It is primarily a carbon-hydrogen-oxygen containing polymer.

Isolation of the additive from kerosene solution leads to structural changes (measured from molecular weight parameters); and mechanical stresses from grinding and "paddle wheel" rotational shear stresses also alter the observed molecular weight characteristics.

Surface tension measurements do not exhibit any fundamental changes as a function of mechanical stress. This could be due to either:

1. The system relaxes too fast to allow observation of potential changes

2. We applied insufficient stress (use of a magnetically driven paddle-bar)

3. There are no observable changes induced in this parameter by mechanical stressing of the system.

Viscosity data are expected changes and mirror those observed by other groups. No attempts are being made at this time to investigate fully the shear-stress induced changes in viscosity coefficients themselves, merely to measure a "limiting" viscosity for infinitely small shear stresses.

Specific-gravity measurements reflect the small concentrations of the FM9 in solution, and it is not surprising that a 0.3% solution does not differ significantly from the specific-gravity of the bulk itself.

Thermal stability measurements provided routine assessments of the solid FM9 properties with respect to degradation, and an estimate of the freezing point range was -47°C to -42°C at 0.3% w/v concentration.

Initial UV/visible absorption spectra would seem to deny any possibility of detecting fuel deterioration over long term storage; but more data needs to be accumulated for solutions made from genuine solid FM9 materials, and not for solids isolated from fuels that have been re-dissolved in other solvents.

B. Characterization of Polyisobutylene

Viscosity Measurement

Viscosity of high molecular weight polymer is a function of temperature, concentration and shear stress (shear rate) in a specific solvent. The viscosity of several high molecular weight polyisobutylene has been studied in toluene at 30°C with different concentrations. A calibrated Cannon-Ubbelohde viscometer (50 E719) was used in this study. ICI have found that when the polymer has a molecular weight of above 10^6 (viscosity average) or an intrinsic viscosity of greater than 2.5 dl/g, a marked reduction in shock dissemination of the solution was obtainable at polymer concentrations as low as those in the critical regions where there was an upturn in the log/log plots of viscosity (apparent at zero shear rate) against concentration.[1] We were not equipped to measure zero shear rate viscosity. The viscosity measured in our system had a very small shear rate and was plotted against concentration. An upturn in the log/log plots was observed at 0.107 to 0.12 W/W% for Old B230 and New B230 polyisobutylene, respectively (Figures 7 and 8). Old B230 and New B230 are two different batches of B230 sample received from BASF.
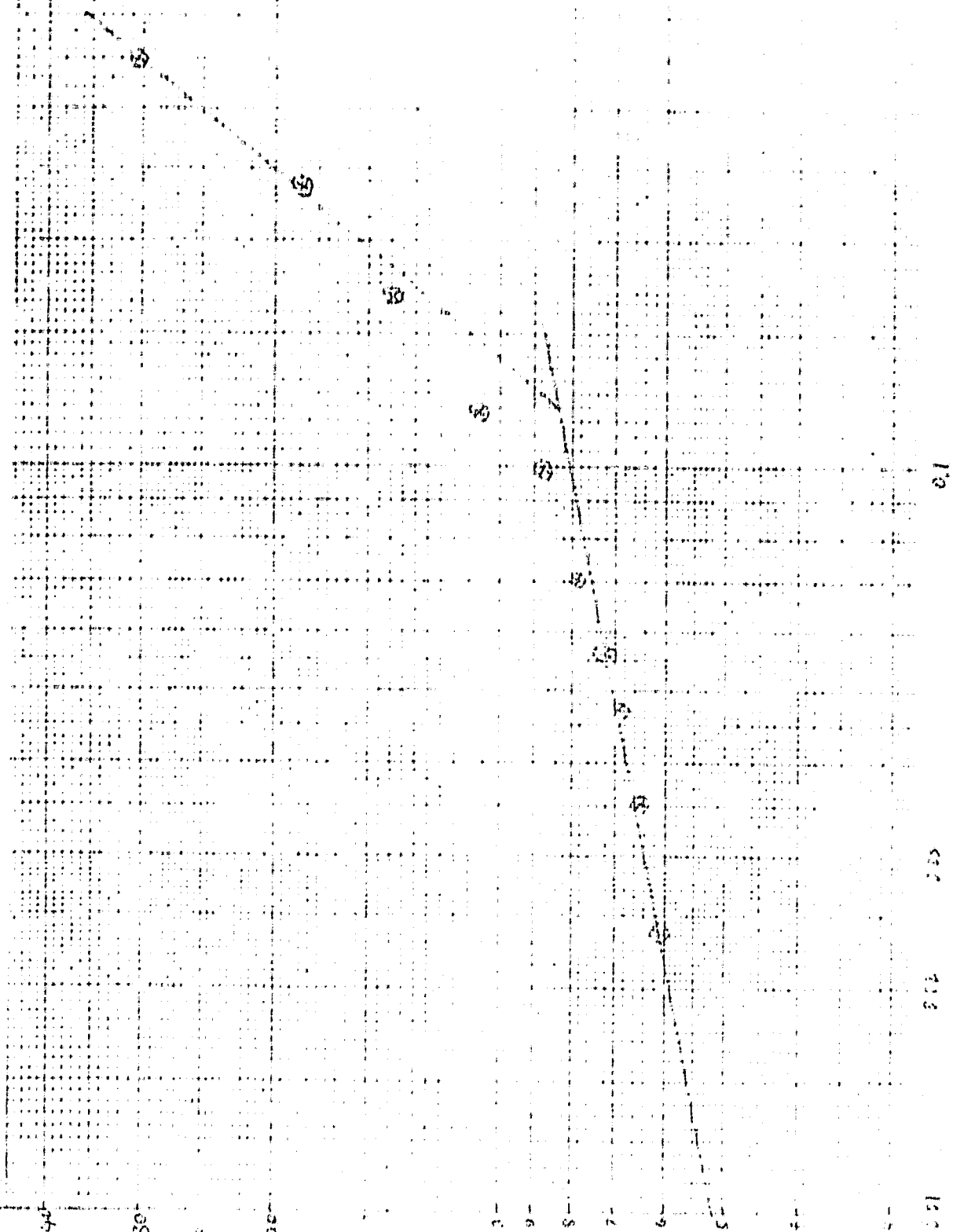
Fig. . Chi ress of the log of viscosity vs concentration in toluene at .
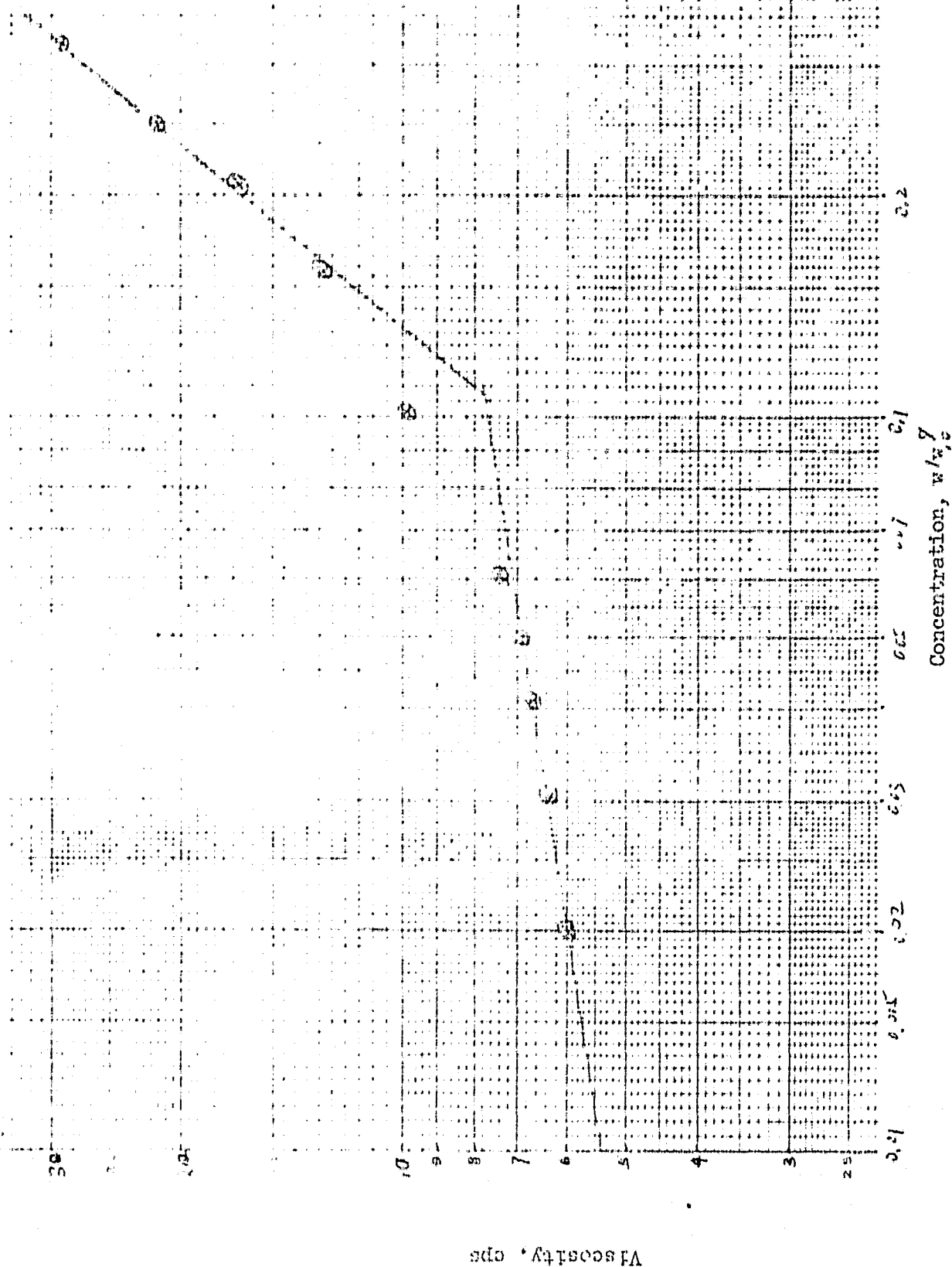
Concentration, w/w, %

Viscosity, cps

Fig. 5. New E230 log/log plot of viscosity vs concentration in toluene at 30°C

Intrinsic viscosity of high molecular weight polyisobutylene samples were measured carefully in toluene at 30°C in the concentration range of 0.1g/100 ml to 0.02g/100 ml. The plots of concentration vs reduced or inherent viscosity for polyisobutylene samples is shown in Figure 9. The viscosity average molecular weight was calculated from Mark-Houwinck equation: $[\eta] = 2\times10^{-4}M^{0.67}$. The viscosity and molecular weight data are shown in Table 3. B230 ppt V and B230 ppt IB are samples precipitated from 280 ml 0.5% new B230 toluene solution by adding methanol of 100 ml and 50 ml respectively. Both B230 ppt V and B230 ppt IB have higher intrinsic viscosity and molecular weight than the unprecipitated new B230 sample. B230 ppt IB which was precipitated from new B230 by adding less methanol (only 20% solid was collected from new B230 solution), has a higher intrinsic viscosity and molecular weight than B230 ppt V. The viscosity average molecular weight of the six samples measured are in the range of $4-6.5\times10^{6}$.

Viscosities at different temperatures for polyisobutylene samples in Jet A fuel have been studied. The results are shown in Figure 10.

Molecular Weight Distribution

Molecular weight distribution of polyisobutylene samples were measured using a Water Associates Model 202 Gel Permeation Chromatograph. The experimental conditions were as follows: solvent, tetrahydrofuran; temperature, ambient; columns, 10^{6}, 10^{5}, 10^{4} Å ustyragel; sample concentration, 0.1%; flow rate, 1 ml/min; detector, reflective index. GPC curves for various polyisobutylene samples are shown in Figure 11. The weight average molecular weight, number average, Z average molecular weight and the dispersitivity were calculated from the GPC curve which was calibrated with polystyrene standards with narrow distribution. The data are shown in Table 3.
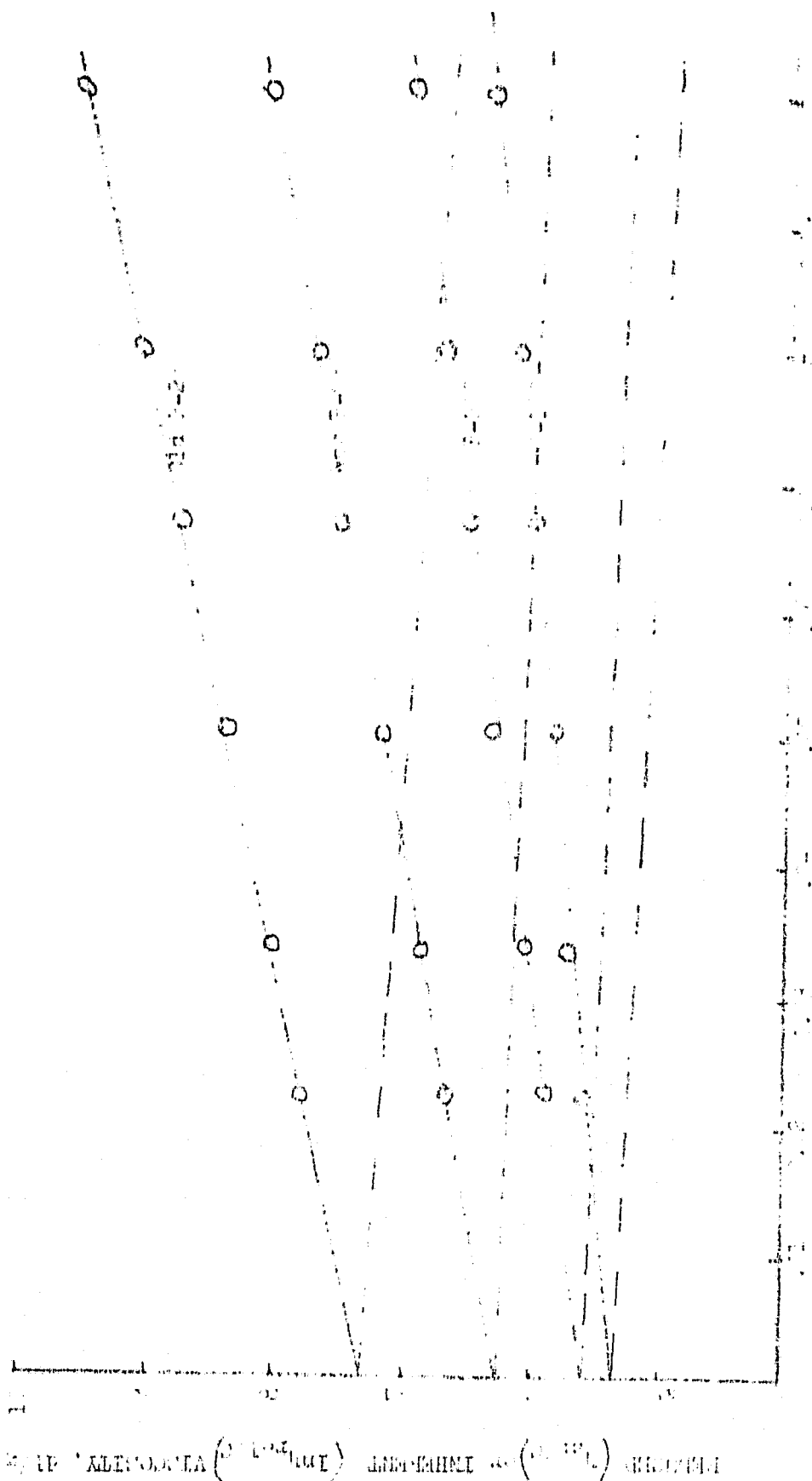
Table 3. Molecular Weight and Molecular Weight Distribution

Sample	$[\eta]$	M_v	M_w	M_n	M_w/M_n	M_z
				GPC		
L160	5.4	4.13×10^6	879K	386K	2.28	1398K
B200	5.6	4.34×10^6	760K	293K	2.59	1303K
New B230	6.3	5.17×10^6	825K	367K	2.25	1323K
B230 ppt V	6.8	5.8×10^6	853K	331K	2.58	1455K
B230 ppt IB	7.05	6.12×10^6	956K	495K	1.94	1423K
Old B230	7.3	6.4×10^6	1030K	531K	1.94	1508K

Figure 10. VISCOSITY OF 3% LIGHT CRUDE-ICE WATER IN FOR A AT DIFFERENT TEMPERATURE
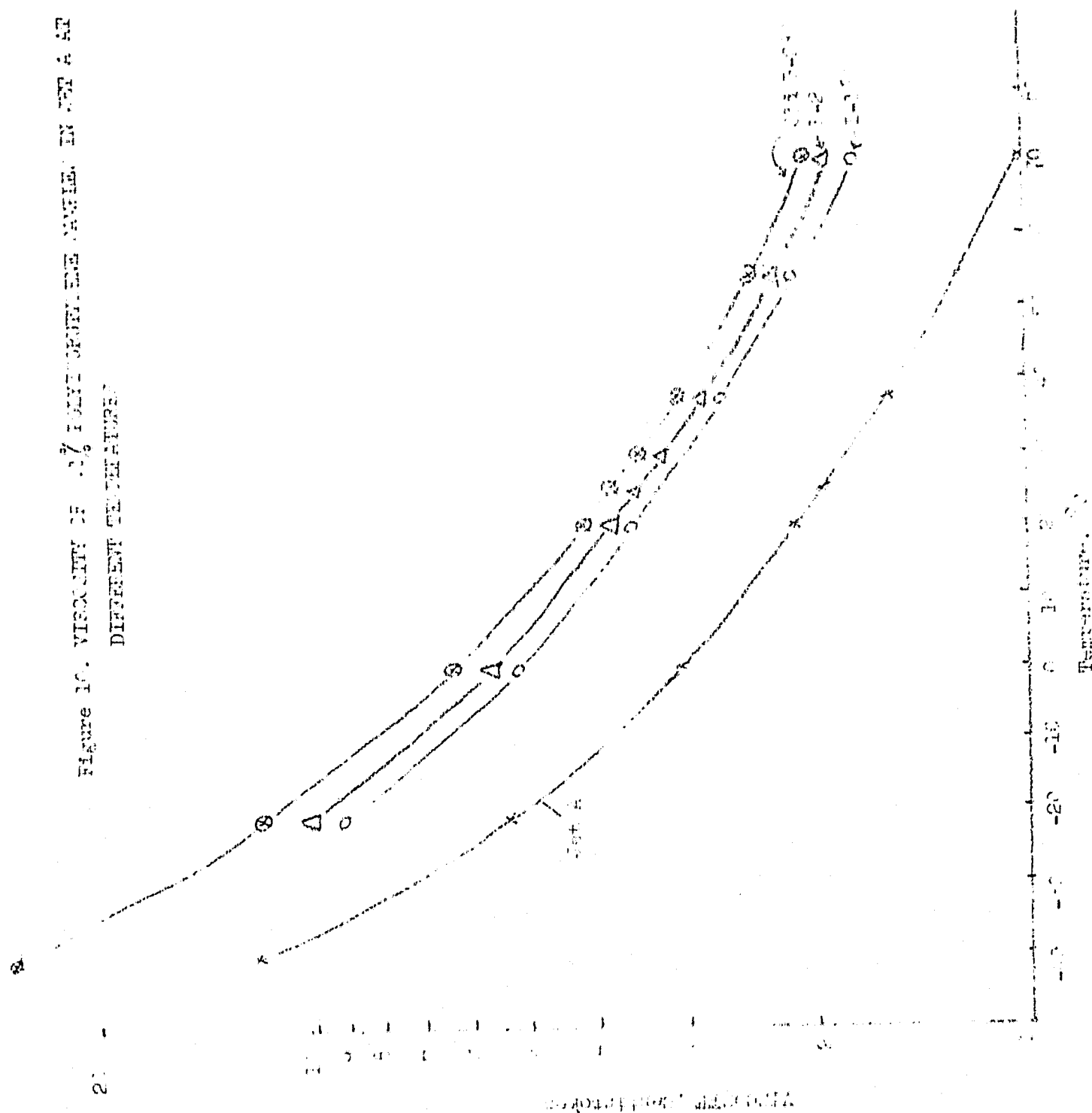
(High molecular weight)   Elution time, min   (low molecular weight)
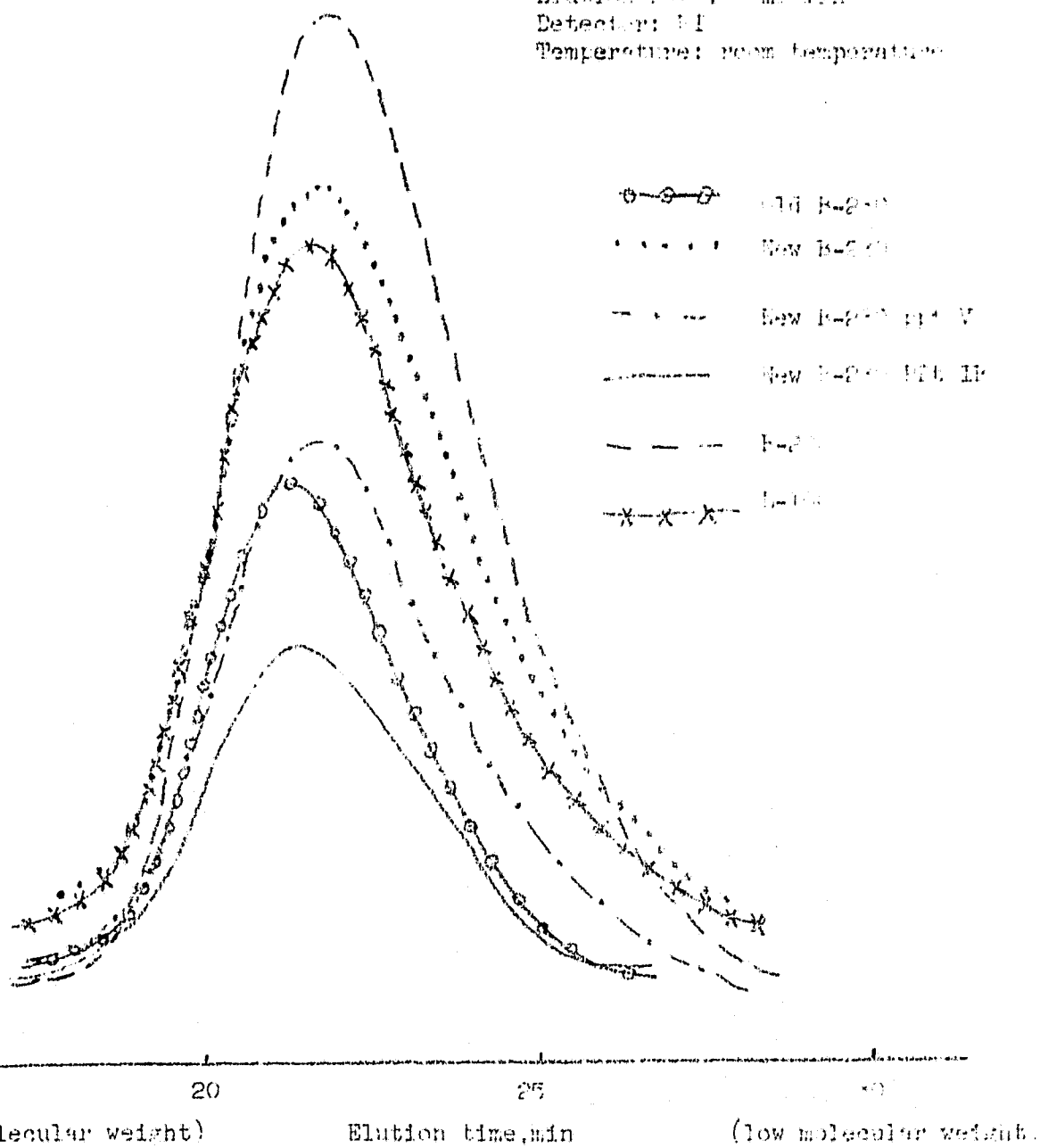
Except for sample L-160, GPC data and intrinsic viscosity data agree to each other very well. The intrinsic viscosity data showed that L160 had the lowest average molecular weight. The GPC data showed that L160 had a higher average molecular weight than B230 ppt V. The unusual results for L160 can be explained as:

1. L160 may be a branched polyisobutylene.

2. L160 may contain a small fraction of low molecular weight material which was not detected by GPC.

C. Misting Characterization of Antimisting Additives

The "misting" characteristic of polyisobutylene and FM-9 in Jet A solution and Jet A were tested by dropping 10 ml samples in a thin stream from a height of 2 meters into a hollow cylindrical vessel. A filter paper ring of 17 cm in diameter and 21 cm in height was standing inside the vessel. A soluble dye was added to each sample. The density of the spots produced on the paper by droplets splashed from the solution gave a comparison of dissemination of the liquid by impact with the base of the vessel. The results are shown in Table 4. FM-9 sample was diluted from aged 1.5% solution which may be degraded. The antimisting characterization can be determined by this simple screening test for AMK candidates. It can be seen that the higher the molecular weight the better the antimisting property for AMK candidates.

TABLE 4

"MISTING" CHARACTERIZATION OF THE AMK SOLUTION BY DROPPING TEST

SAMPLE		CONC WT %	% AREA SPLASHED
FM-9 (AGED)	1.47	0.05	80
		0.2	30
		0.3	9
		0.4	NONE
C288	1.07	1.8	30
		0.72	95
L160	5.4	0.057	15
		0.114	12
		0.228	NONE
B200	5.6	0.015	17
		0.04	7
		0.08	NONE
OLD B230	7.3	0.006	20
		0.013	5
		0.031	4
		0.05	3
		0.06	0.5
		0.07	NONE
JET A			100

D. Degradation Study of Antimisting Additives

Room temperature mechanical degradation of 0.3% FM-9 and 0.1% polyisobutylene (Old B230) in Jet A was studied by stirring the solution with a rotating paddle at 450 RPM. Sample was taken out at different time interval and the intrinsic viscosity of the stirred solutions was measured at 30°C in Jet A. The results are shown in Figure 12. Both FM-9 and polyisobutylene were degraded by stirring and the rate of the degradation for both samples was competitive.

References

1. D. W. Osmond, N. D. Smith and F. A. Waite, U. K. Patent No. 1259113 (1972).

2. J. Brandrup and E. H. Immergut, Polymer Handbook, IV-8, Interscience Publishers, NY (1966).

Figure 19

VISCOSITY DEGRADATION OF WATER BASE MUD AT ELEVATED TEMPERATURE
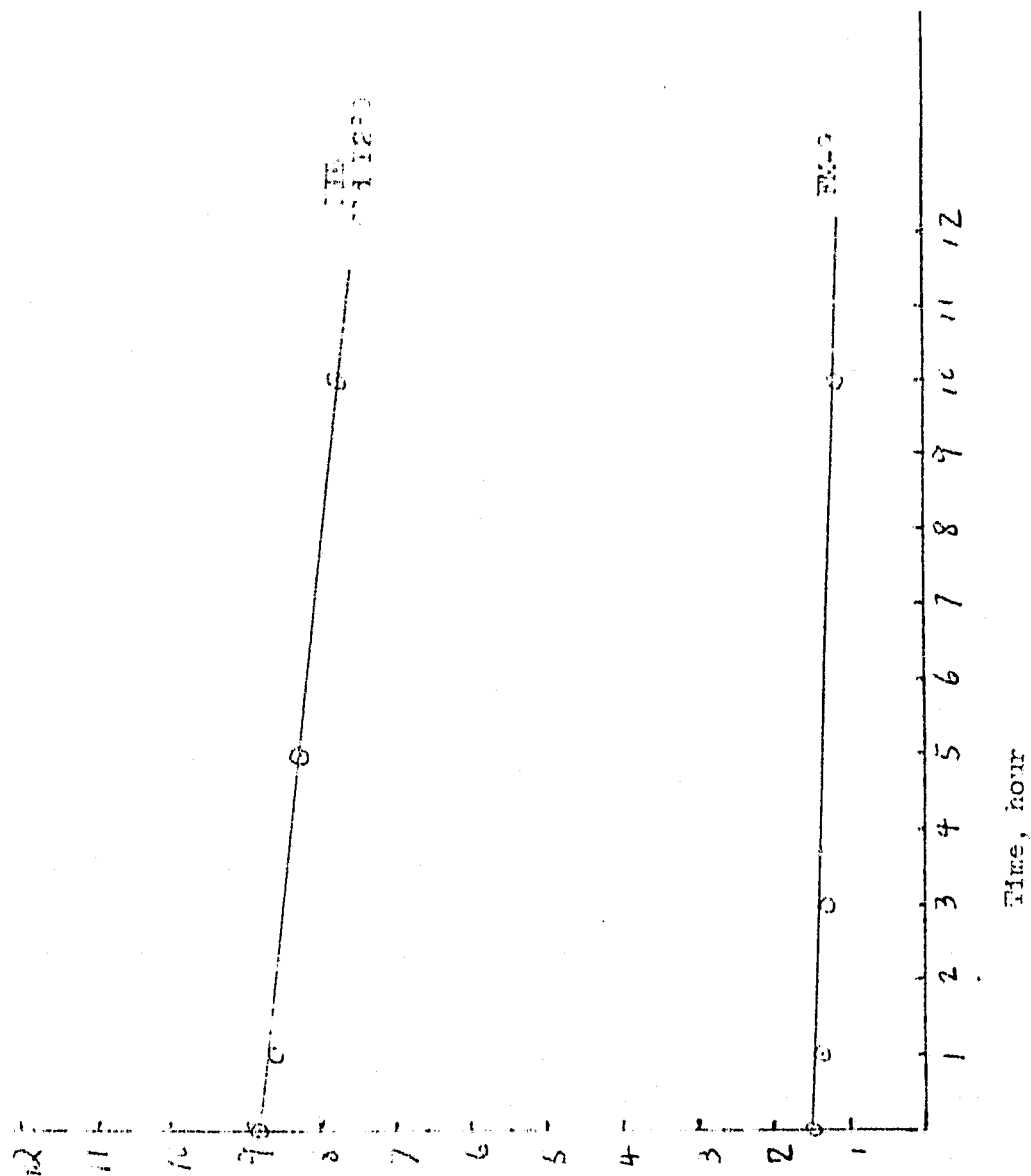
(AS FUNCTION OF BODY TEMPERATURE)

Table I. Intrinsic Viscosity of In-House Polyisobutylene and Polyisobutylene-
Polypropylene Copolymer

Sample	Conc. Range (g/100 ml)	$[\eta]$ dl/g	Mv
C_{286}	0.13-0.37	0.37	7.5×10^4
C_{287}	0.10-0.31	0.82	2.5×10^5
C_{288}	0.1 -0.3	1.07	3.7×10^5
C_{289}	0.12-0.35	0.5	1.2×10^5
C_{291}	0.24-0.7	0.36	7.3×10^4
$*C_{303}$	0.15-0.44	0.41	8.7×10^4
$*C_{304}$	0.16-0.5	0.51	1.2×10^5
$*C_{305}$	0.2 -0.65	0.34	6.6×10^4
C_{307}	0.13-0.43	0.68	1.87×10^5
C_{309}	0.12-0.41	0.62	1.62×10^5
C_{310}	0.16-0.49	0.78	2.29×10^5

*Copolymer

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Synthesis of Poly-1-Alkenes

Hexene - 1. Octene - 1. Decene - 1, and Dodecene - 1 were polymerized by the Ziegler - Natta catalyst ($R_3Al + VOCl_3$) in heptane at 0°C. The intrinsic viscosities of their polymers are listed in Table II.

Table II.   Intrinsic Viscosity of Poly-1-hexene,   Poly-1-octene, Poly-1-decene, and Poly-1-dodecene.

Sample	Structure	[η] dl/g
C330	poly-1-hexene	3.2
C331	poly-1-hexene	3.1
C332	poly-1-hexene	2.8
C333	poly-1-hexene	3.2
C334	poly-1-hexene	3.3
C335	poly-1-hexene	2.1
C336	poly-1-hexene	4.0
C337	poly-1-hexene	3.3
C350	poly-1-hexene	3.5
C351	poly-1-hexene	3.8
C339	poly-1-octene	2.7
C340	poly-1-octene	2.8
C341	poly-1-octene	3.0
C342	poly-1-octene	5.4
C343	poly-1-decene	4.7
C364	poly-1-decene	4.7
C346	poly-1-decene	5.5
C347	poly-1-dodecene	3.1
C348	poly-1-dodecene	5.3
C349	poly-1-dodecene	4.3

PHASE TWO

Phase two of the Cooperative Agreement was concerned with the characterization and degradation of composite resins.

A. Characterization and Degradation of Phthalocyanine and its Derivatives

Mass spectrometry of phthalocyanine (PC) was studied on a Hewlett-Packard MS 5984 by direct introduction at 70 eV. The parent peak was at m/e 514 and the fragmentation peaks were at m/e 128 and 103. PC was pyrolyzed at 500°C and 800°C in a CDS pyroprobe solid pyrolyzer, which was connected with Hewlett Parkard GC/MS. The major pyrolysis product was dicyanobenzene. The minor products were cyanobenzene, benzene, toluene, hydrogen cyanide, ammonia and Metal (Cu, Co, Zn, Ni) derivatives of PC were stable and nonvolatile. No fragmentation peak, parent peak and volatile products were detected by heating the samples up to 500°C. Metal phthalocyanine tetracarboxylic acids gave off carbon dioxide at above 350°C. Pyrolysis GC/MS on the metal(II) 4,4',4",4'''-phthalocyanine trtraamines cured epoxy novolac resins was studied at 800°C. Major degradation products were derived from the epoxy resin. A manuscript has been under preparation.

B. Thermal Oxidation of Epoxy Resin

Epoxy/graphite panel (3501-GAS) was exposed to flux level of 2.5 W/cm^2 in a NASA-Ames radiant panel fire simulator in flame and non-flame mode[1]. Toxic gases of hydrogen cyanide and hydrogen sulfide were collected in 20 ml scrubbing solution of 0.1 M NaOH. The cyanide and sulfide ions were analyzed by Dionex ion chromatography using the following eluent: 0.002 M Na_2CO_3, 0.0025 M $Na_2B_2O_7$,

0.0025 M NaOH and 1 ml of ethylene diamine per liter of solution. The concentration of oxygen, carbon dioxide, carbon monoxide and organic gases in the radient panel chamber were analyzed by gas chromatography using columns packed with molecular sieve or chromosorb 102. Organic volatiles were collected in a cold trap and then analyzed by GC/MS[2]. The analytical results are shown in Tables 5,6 and 7. Very little organic volatiles were produced in the flame mode. Only trace amounts of hydrogen cyanide was generated in the non-flame mode. The production of hydrogen cyanide in the flame mode was probably from combustion of nitrogen containing organic volatiles.

C. Thermal/Aging Study of Composite Resins

Thirteen cured graphite composites were thermally aged at $177^{\circ}C$ in a forced air furnace and studied by weight loss and DMA measurements. Sample name, sample id number and graph symbol are listed in Table 8.

The weight of the composite (five 2.4 x 1.3 x 0.13 cm pieces for each composite) was measured before aging. The samples were taken out periodically for weight loss measurements and room temperature flexural youngs modulus measurements during aging.

Data are shown in figures 13 - 19. Figures 13,14 and 15 are the weight loss data. Most of the composites showed a fast initial weight loss rate due to loss of absorbed water and solvents. After the initial fast weight loss, the cured graphite composite composites showed a constant weight loss rate due to thermal oxidation. Figures 16 - 19 are the modulus data for the aged composites. The modulus decreased after aging. PSP was the most stable composite. Epoxy 934 was the least stable composite.

References

1. Ming-ta S. Hsu, Annual Report on NASA Cooperative Agreement No. NCC-28, September 1981.

2. Ming-ta S. Hsu, "Analytical Methods for Toxic Gases from Thermal Degradation of Polymers", J. of Combustion Toxicology, 4, 293 (1977).

Table 5 . Gas Analysis of 3"x3" 3501-GAS Panel in a Radiant Panel Test -
Flame Mode

Time (sec)	O_2%	CO_2%	CO (ppm)	$\overline{CN}$(ppm)	$S^=$(ppm)
90	18.46	2.14			
180	18.23	2.24			
200-220				51	19
300	16.94	3.33	2220		
420	16.98	3.40	2700		
440-460				80	442
630	17.05	3.41	2940		
660-680				72	366
840	17.16	3.30	2980		
880-900				95	340
1020	17.47	3.19	3110		
1100-1120				106	183
1200	17.60	3.15	2300		

Table 6. Gas Analysis of 6"x6" 3501-GAS Panel in a Radiant Panel Test -
Nonflame Mode

Time (sec)	O_2%	CO_2%	CO %	CH_4 (ppm)	Other Organic Gases %	CN^- (ppm)	$S^=$ (ppm)
90	19.82	0.99	-	-			
180	19.62	0.99	-	-			
200						5.3	13
300	19.53	1.37	0.175	150	0.172		
350						10.6	883
420	18.01	1.92	0.58	1.10	0.468		
500						5.3	1281
630	16.08	2.41	1.066	2630	0.811		
680						5.3	1016
830	15.32	2.41	1.259	3360	0.811		
900						trace	592
1020	15.35	3.01	1.291	3340	0.797		
1120						trace	212
1190	15.49	3.04	1.102	3100	0.72		

Table 7 . Organic Volatiles Generated from 6"x6" 3501-GAS Panel From Radiant
Panel Test in a Nonflame Mode

	Concentration in Gas Form			
Organic Volatile	Trap 1 (400-700 sec) mg/1	ppm	Trap 2 (800-1200 sec) mg/1	ppm
Toluene	3.26	793	0.243	59
Aniline	0.927	223	0.161	39
P-toludine or N-methyl aniline	0.226	47.3	0.077	16
N-Dimethyl aniline	0.137	25	0.034	6
N-Et aniline	0.076	14	0.036	6.6
Isoquinoline	0.146	25	0.079	14
Indole	0.047	8	0.02	3.5
Methylquinoline	0.229	36	0.113	17.7
Diphenylamine	0.056	7.4	0.046	6
Diphenyl methylamine	0.04	5	0.014	2

Table 8. Composite Samples for Thermal/Aging Studies

Sample id Number	Graph Symbol	Sample Name
R-1 EpoxyB	1	Pan #1 Epoxy Hitco #7-9 NASA # 1021B
R-2 Benzyl	2	Pan #8 Benzyl
R-3 PSP	3	PSP 6024M/W133
R-4 Imide8	4	Pan #7 Polyimide Celion 6000/ V378A Hitco #8-9
R-5 EpoxyD	5	Pan #1 Epoxy Hitco #7-9 NASA # 1021D
R-6 Imide6	6	Pan #7 Polyimide Celion 6000/ V378A Hitco #6-1
R-7 Xylok	7	Pan #5 Xylok 210
R-8 H795	8	Pan #8 Celion 6000/H795 BMI
R-9 934	9	Epoxy Celion 6000/934
R-10 5208	E	5208/133 8 Harness Satin
R-11 AR98	A	AR-98 BT
R-12 CTBN10	B	AR-101 10% CTBN
R-13 CTBN2	Ɛ	AR-111 2% CTBN
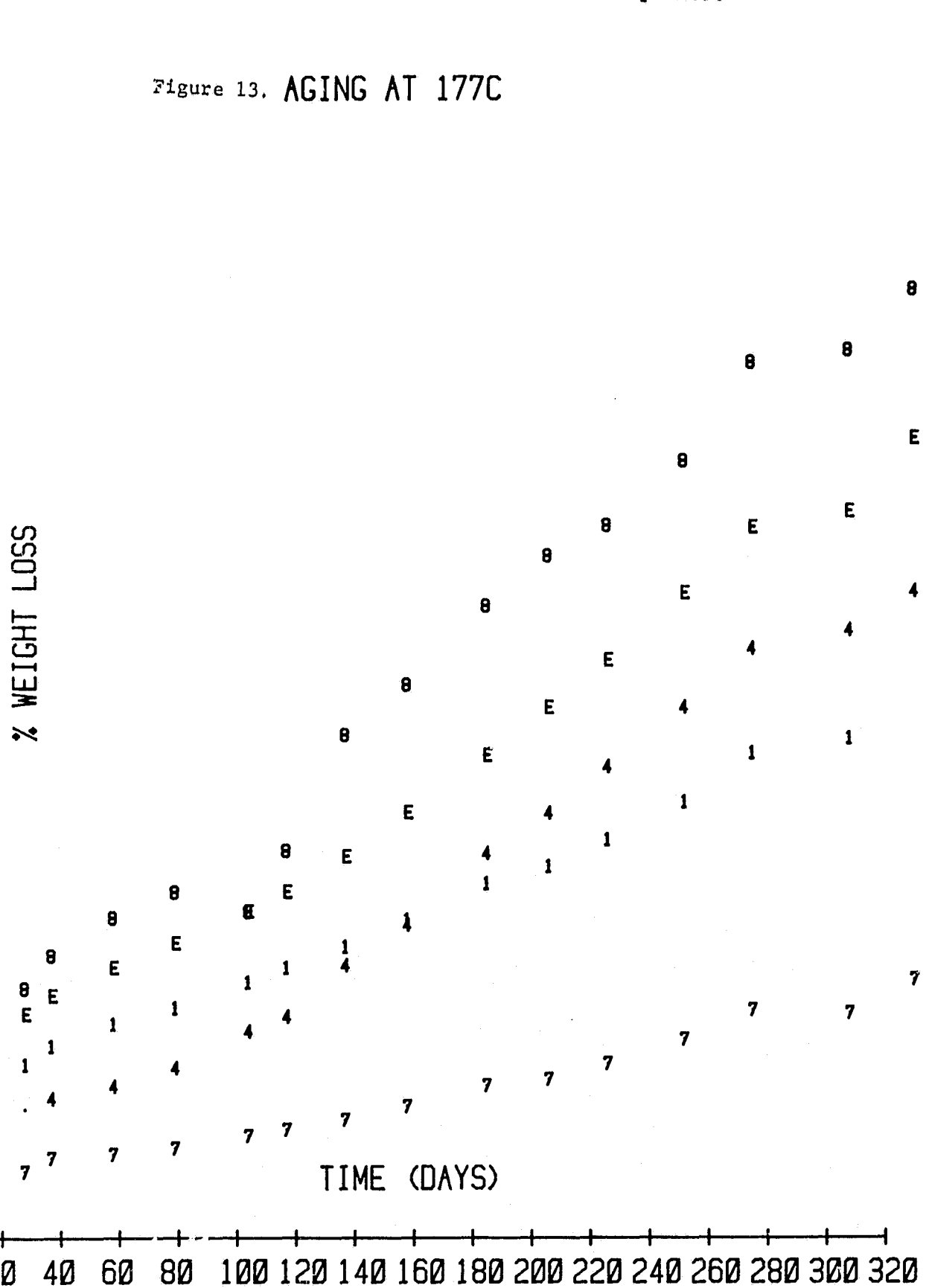
Figure 13. AGING AT 177C

Figure 14. AGING AT 177C
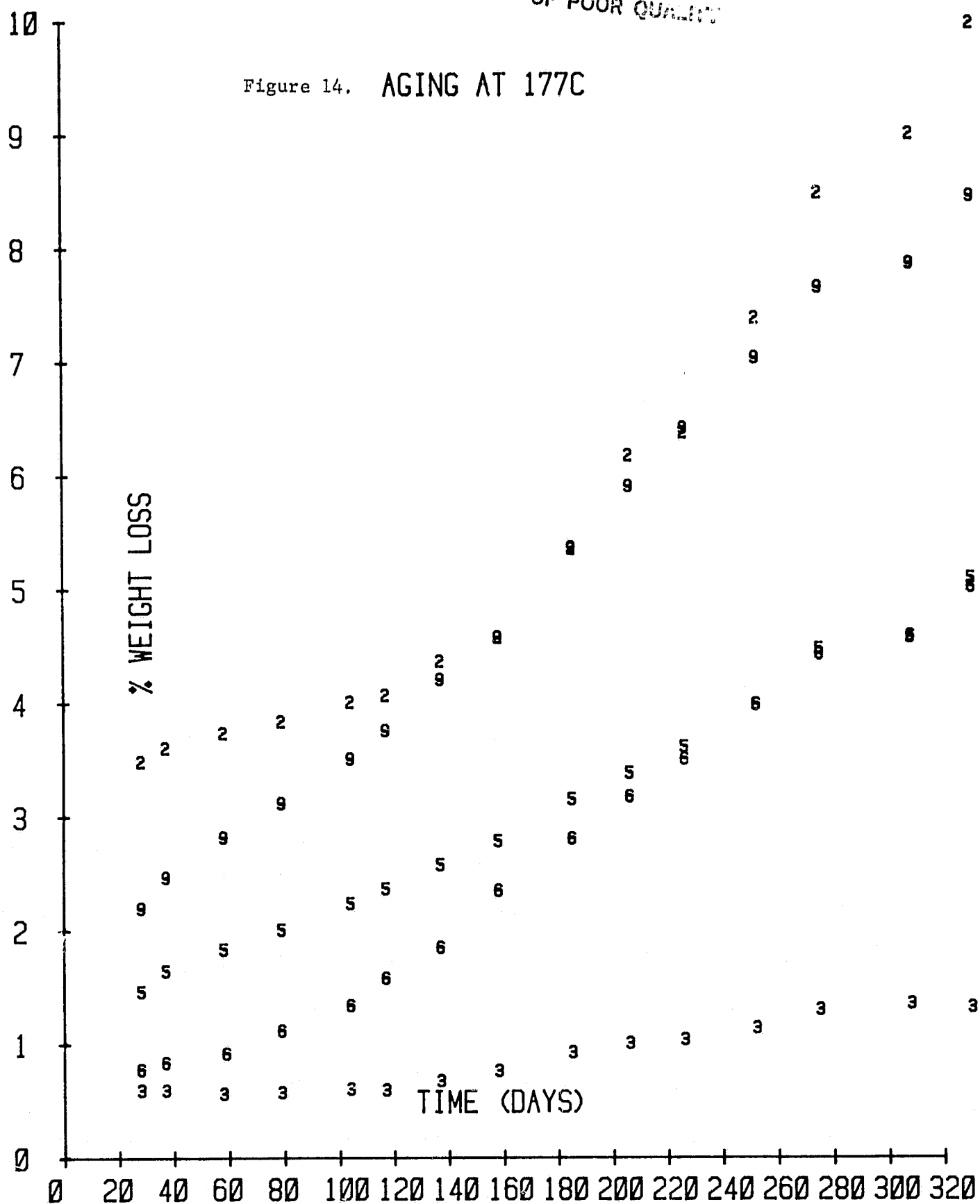
Figure 15.   AGING AT 177C
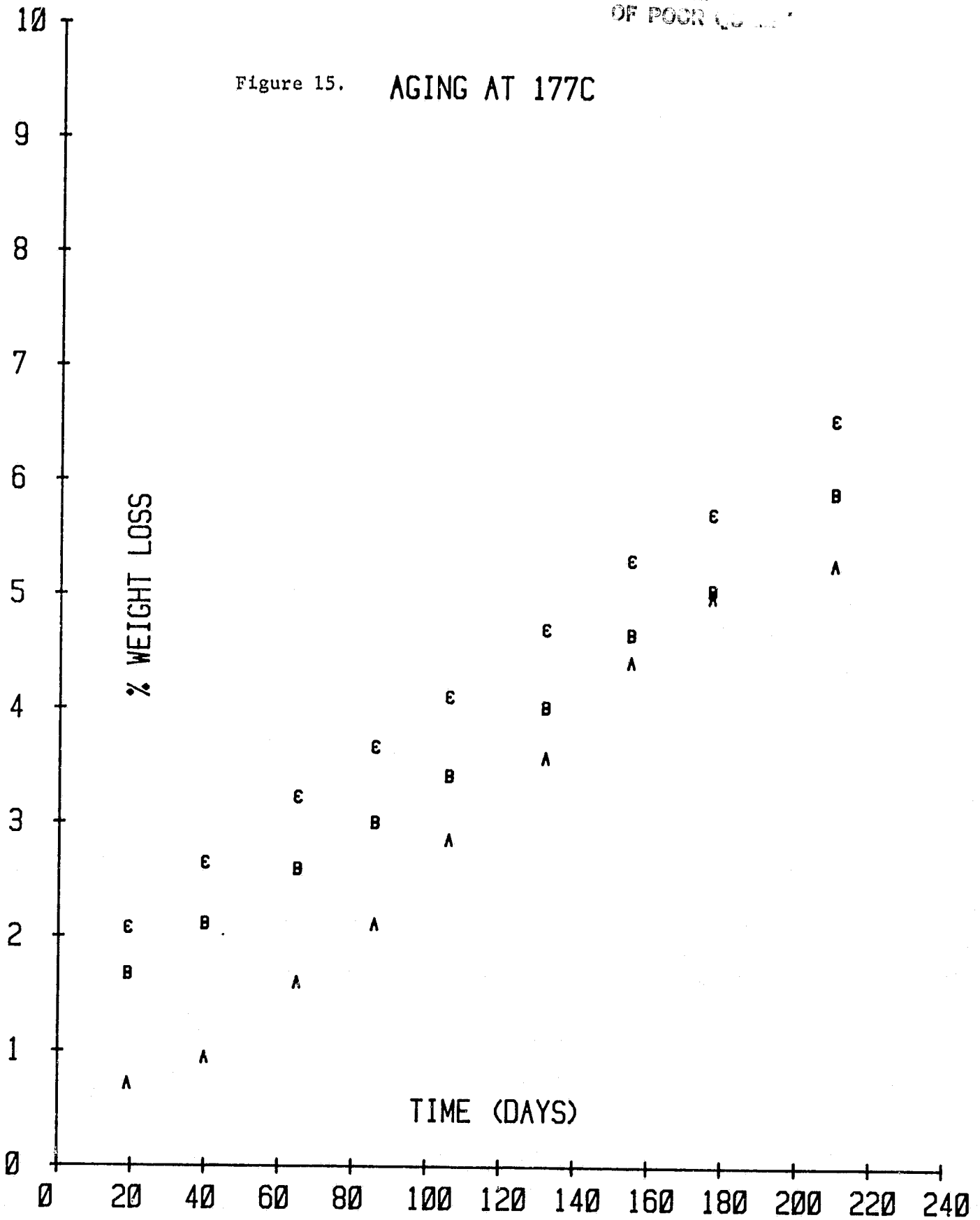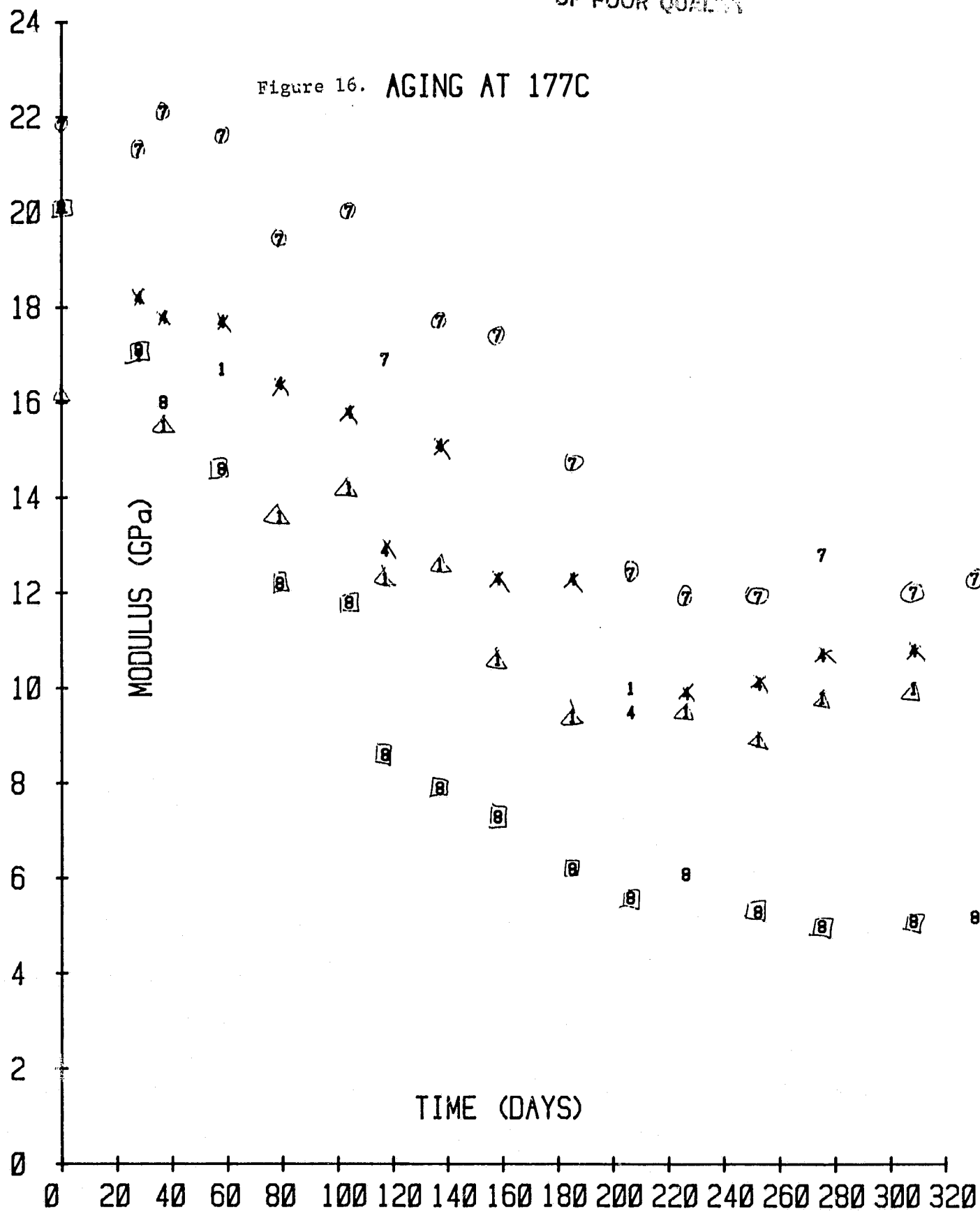
Figure 16. AGING AT 177C

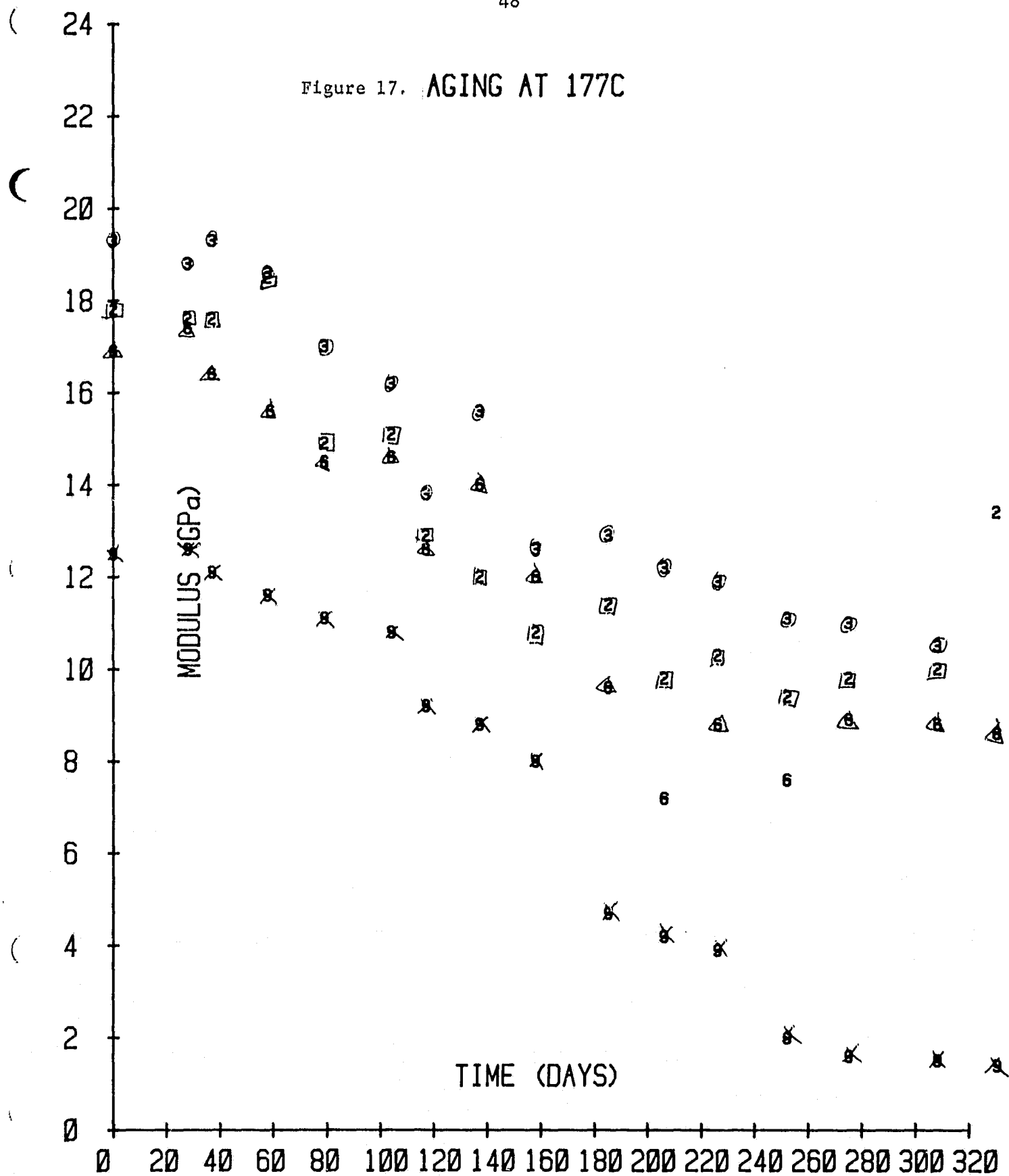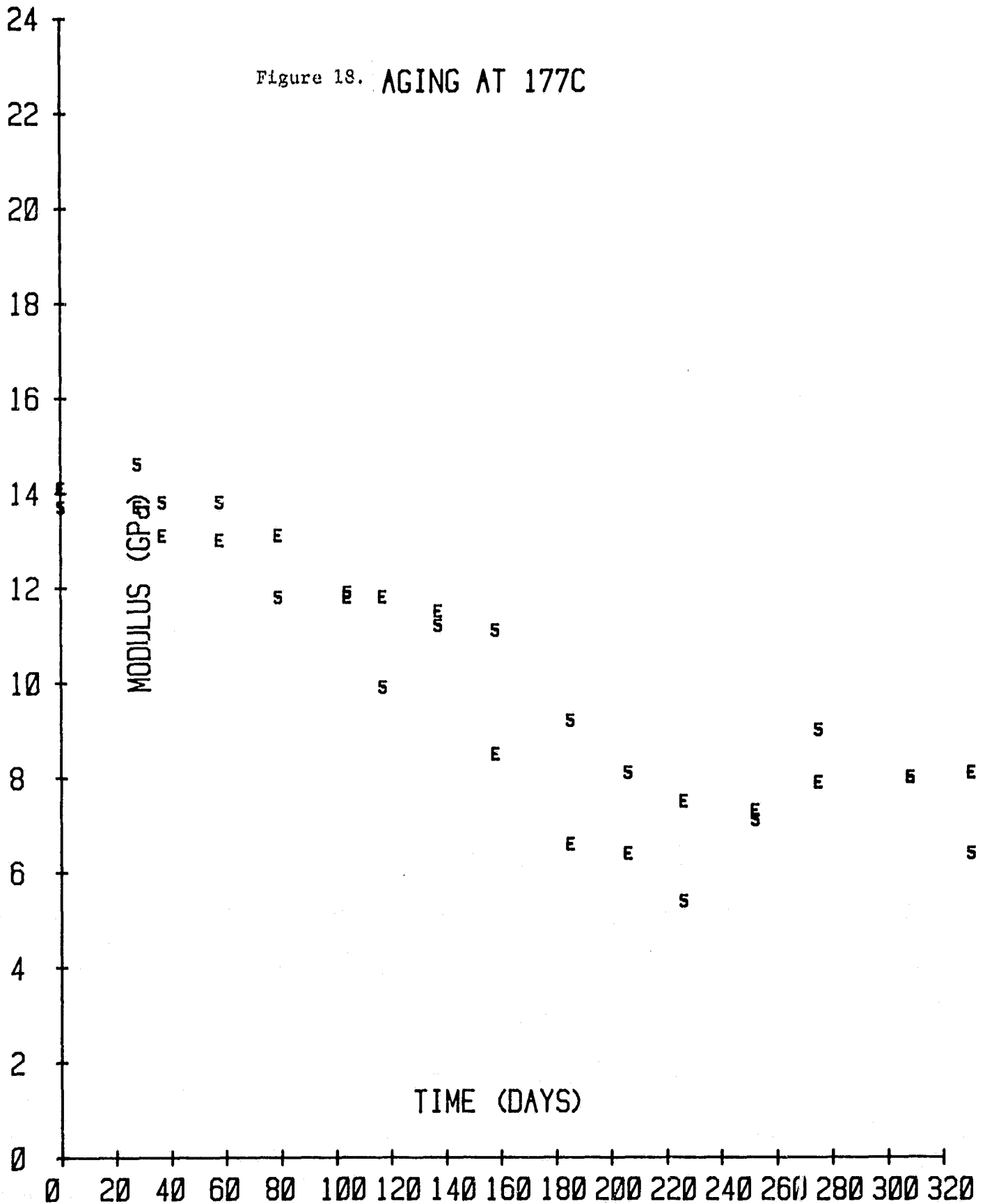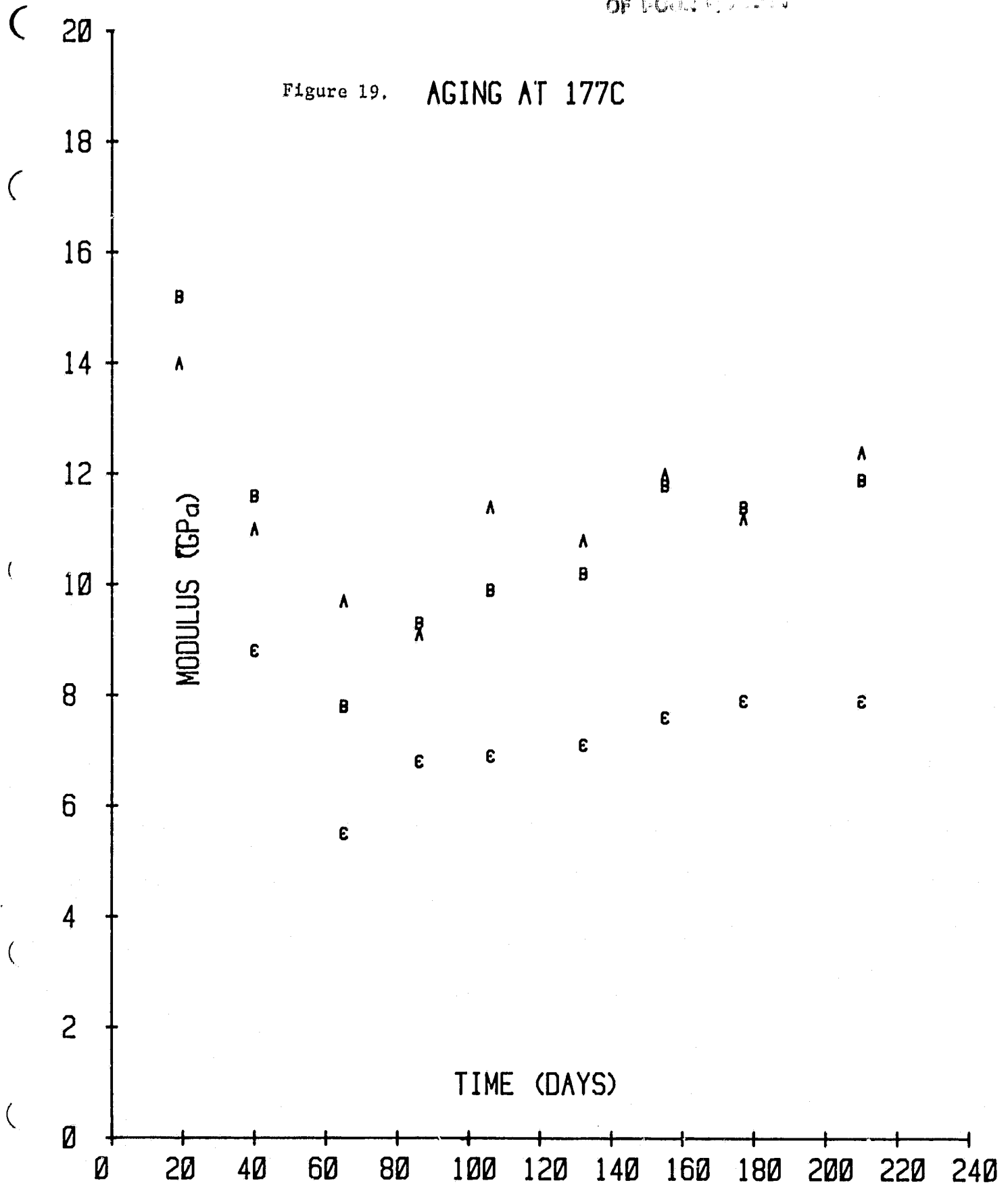Figure 17. AGING AT 177C

Figure 18. AGING AT 177C

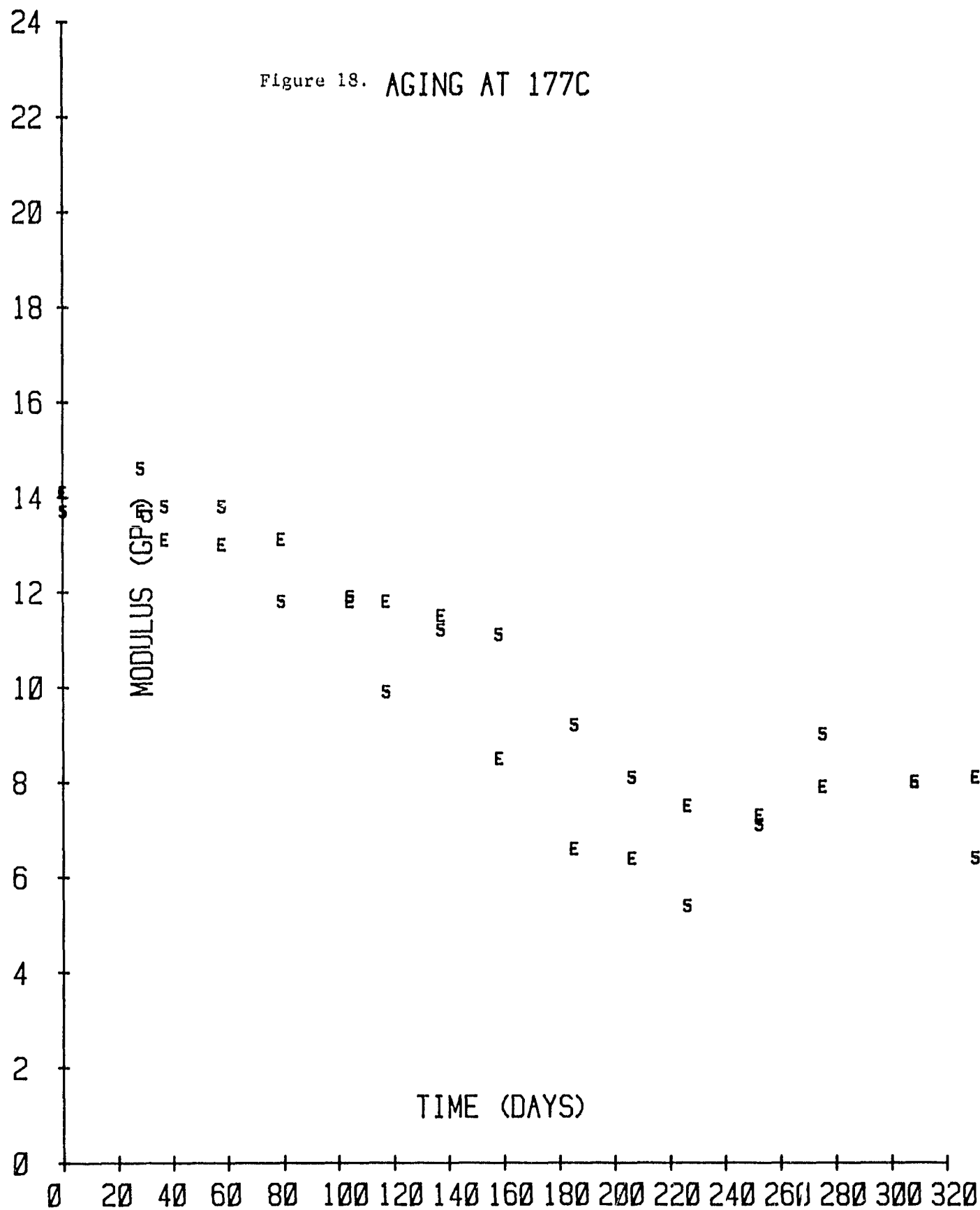Figure 19. AGING AT 177C

Figure 18. AGING AT 177C

Figure 19. AGING AT 177C

MODULUS (GPa)

TIME (DAYS)